ISSN 1070-3632, Russian Journal of General Chemistry, 2013, Vol. 83, No. 11, pp. 2005–2017. © Pleiades Publishing, Ltd., 2013.
Original Russian Text © L.P. Stepovik, A.Yu. Potkina, A.I. Poddelskii, 2013, published in Zhurnal Obshchei Khimii, 2013, Vol. 83, No. 11, pp. 1805–1818.

Oxidizing Properties of the *tert*-Butyl Hydroperoxide–tetra-*tert*-Butoxychromium System

L. P. Stepovik[a], **A. Yu. Potkina**[a], **and A. I. Poddelskii**[b]

[a] *Lobachevsky Nizhni Novgorod State University, ul. Gagarina 23, Nizhni Novgorod, 603950 Russia*
e-mail: lstepovik@mail.ru

[b] *Razuvaev Institute of Organometallic Chemistry, Russian Academy of Sciences, Nizhni Novgorod, Russia*

Received November 19, 2012

Abstract—*tert*-Butyl hydroperoxide reacts with the tetra-*tert*-butoxychromium by oxidizing the latter to chromyl $Cr^{V}=O$ (C_6H_6, 20°C). At *t*-BuOOH–Cr(OBu-*t*)$_4$ ratio of 2 : 1 or higher, oxygen is released. The occuring processes include the formation of chromium-containing peroxides and peroxytrioxydes. The *t*-BuOOH–Cr(OBu-*t*)$_4$ system oxidizes aromatic hydrocarbons of various structures (anthracene, 9,10-dimethylanthracene, 1,1-diphenylethylene, alkylarenes), as well as primary and secondary alcohols. Depending on the structure of the substrate, the oxidants are: in situ generated oxygen including that in the singlet state, peroxy radicals, or chromium-containing peroxides.

DOI: 10.1134/S1070363213110066

Complex or inorganic derivatives of Cr(III) and Cr(VI) are applied in hydroperoxide oxidation of organic compounds [1, 2]. To the very best of our knowledge, no data has been available on the use of chromium alkoxides in oxidizing systems, and information on Cr(IV) complexes as oxidation catalyst has been limited. Chromium oxide *meso*-tetraphenylporphyrinate is known to oxidize benzyl alcohol to benzaldehyde, but it does not catalyze alkanes hydroxylation. $C_5H_5NHCrO_2X$ complexes (X = Cl or F) in combination with *tert*-butyl hydroperoxide convert secondary alcohols as well as propargyl and benzyl methylene groups into ketones with high yield [1].

Recently, the combined oxidation systems of *tert*-butyl hydroperoxide (**I**) and transition metal (titanium [3], zirconium [4], vanadium [5]) *tert*-butoxide or metal (cobalt, chromium, vanadium [6, 7]) acetylacetonate have been studied. Such systems oxidize organic substrates under mild conditions (20°C). Depending on the substrate structure, metal peroxides, peroxytrioxides, or *in situ* generated oxygen may act as oxidizer.

The aim of this work was to study the interaction of tetra-*tert*-butoxychromium **II** with *tert*-butyl hydroperoxide **I** in an inert solvent, and to estimate the oxidizing ability of the system (hereafter referred to as **I**+**II**) towards alkylarenes and their selected oxygen-containing derivatives. Our preliminary trials revealed that benzene was not oxidized by **I**+**II**.

The reaction of **II** with **I** in benzene (room temperature) was performed at varied molar ratio of **II** : **I**, 1 : 1 to 1 : 10. Starting from 1 : 2 ratio, oxygen evolution was observed (Table 1). The hydroperoxide always reacted quantitatively, being reduced to alcohol. *tert*-Butyl peroxide was identified among the products as well. The reaction was studied by NMR (^{1}H and ^{13}C), ESR, IR, and electronic spectroscopy. The bright sky blue color of **II** was due to the absorption bands of ligands, a doublet with λ_{max} = 635 and 760 nm [8].

After addition of **I** to sky blue solution of **II** (1 : 1), the solution first turned wine-red, instantly changed into blue-green. The electronic absorption spectrum of the reaction mixture under inert was identical to that of the parent compound (in the ligand bands range). However, an additional band appeared at around 400 nm. The spectrum did not change during 24 h. If the reaction was performed in air, the bands of ligand disappeared within 5 min, a new band appeared at 371 nm, and the solution became yellow. The

Table 1. Products of tetra-*tert*-butoxychromium **II** reaction with *tert*-butyl hydroperoxide **I** (C_6H_6, 20°C), in moles per 1 mol of **II**

Volatile fraction [a]	**II**:**I** molar ratio			
	1:1	1:2	1:4	1:10
t-BuOH	1.86	3.48	5.84	11.50
O_2	–	0.57 (0.27[b])	1.32 (0.33[b])	3.30 (0.33[b])
$(t\text{-BuO})_2$	0.05	0.07	0.16	0.43

[a] Averaged. [b] Per 1 mol of the hydroperoxide.

electronic absorption spectra of the reactions mixtures at **II** : **I** ratios of 1 : 4 and 1 : 10 were similar, thus indicating the complete decomposition of the ligand environment of metal. The spectra of volatile fractions were identical to those of the reaction mixtures; in other words, the colored substance condensed with the solvent. Treatment of the volatile fractions with triphenylphosphine led to disappearance of yellow coloration, the band at 371 nm vanished, and triphenylphosphine oxide was formed. Taking into account that chromium compounds containing chromyl group Cr^{V}=O oxidized Ph_3P to Ph_3PO [9–11], the absorption band at 371 nm could be assigned to the Cr=O bond. When the **I** : **II** ratio was increased to 4–10 : 1, in the IR spectra of nonvolatile chromium-containing residue the absorption band at 945 cm^{-1} prevailed. That band, absent in the IR spectrum of the parent compound, was assigned to the Cr^{V}=O bond of chromyl [10].

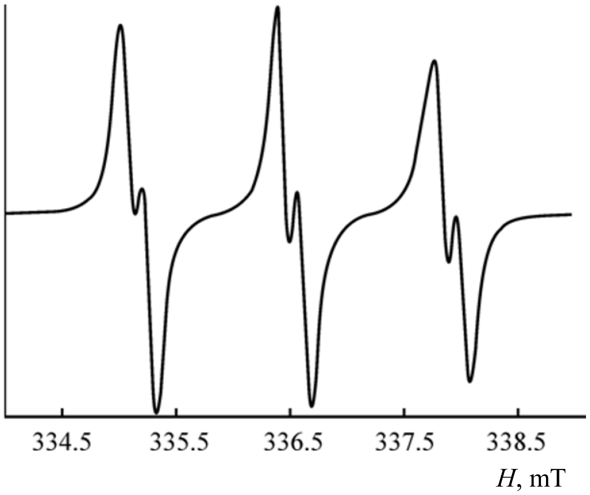


Fig. 1. ESR spectrum of tetra-*tert*-butoxychromium–*tert*-butyl hydroperoxide (1:1) in the presence of *C*-phenyl-*N*-*tert*-butylnitrone (C_6H_6, 20°C).

The reaction of **II** with **I** was studied by ESR in the absence of spin traps and in the presence of 2-methyl-2-nitrozopropane or *C*-phenyl-N-*tert*-butylnitrone. In the absence of the spin traps, regardless of the solvent (C_6H_6, EtPh, 20°C), the ESR spectrum of the reaction mixture (1 : 1) contained a broad singlet with g = 1.961 and ΔH = 9.0 mT. Since **II** was diamagnetic, the recorded signal should likely be assigned to a compound containing Cr(V). In the presence of *C*-phenyl-*N*-*tert*-butylnitrone, immediately after mixing, a triplet was registered with hyperfine coupling constants (HFC) characteristic of the alkoxy radical spin-adduct [a_N = 1.35 mT, a_H = 0.17 mT, g = 2.0052]. However, the HFC constants differed from those of *tert*-butoxide radical [12]. Along with anisotropy of the isotropic spectrum (Fig. 1), that allowed assigning the signal to the spin-adduct of *C*-phenyl-*N*-*tert*-butylnitrone with a chromium-containing alkoxy radical, possibly, with $(t\text{-BuO})_3CrO^{\cdot}$. The spectrum contained a signal with g = 1.970 as well, characteristic of Cr^{V}=O [9, 10], but it was weak.

The ESR spectrum of the reaction mixture (1 : 10, C_6H_6, 20°C) in the absence of spin trap contained a singlet assigned to peroxyl radical (g = 2.015 and ΔH = 1.7 mT). Its intensity decreased with time to disappear within 15 min. In the isotropic ESR spectrum of the same reaction mixture in the presence of 2-methyl-2-nitrosopropane, a signal of peroxyl radical with the same g-factor was observed as well, and a new signal with g = 1.979 was found, assigned to a Cr^{V} ion containing Cr^{V}=O bond (1) [9, 10]. The signal of peroxyl radical decreased with time, while the signal of chromyl increased (Fig. 2), indicating the relationship of those species. Likely, the chromium-containing peroxyl radicals $Cr^{IV}OO^{\cdot}$ are observed. After 25 min, the signal of the peroxyl disappeared; the signal of Cr^{V}=O got stronger, appearing as a singlet of ^{52}Cr (I = 0) (1) with four weak satellites due to another isotope, ^{53}Cr (I = 3/2), $a_i(^{53}Cr)$ = 1.7 mT [9]. Vanishing of the peroxyl radical signal was accompanied with appearance of weak signals of 2-methyl-2-nitrosopropane adducts. In the isotropic spectrum, the following signals were identified: a triplet (1 : 1 : 1, g = 2.0056, and a_N = 2.72 mT) assigned to the adduct of the spin trap with *tert*-butoxy radical, $t\text{-BuN}(O^{\cdot})OBu\text{-}t$ (2) [12]; a triplet with g = 2.006 and a_N = 0.78 mT assigned to the spin-adduct of acyl radical, $RC(O)N(O^{\cdot})OBu\text{-}t$ (3); and a triplet with broadened lines, g = 2.006, and a_N ~ 1.35 mT assigned to the adduct of 2-methyl-2-nitrosopropane with the carbon-centered radical

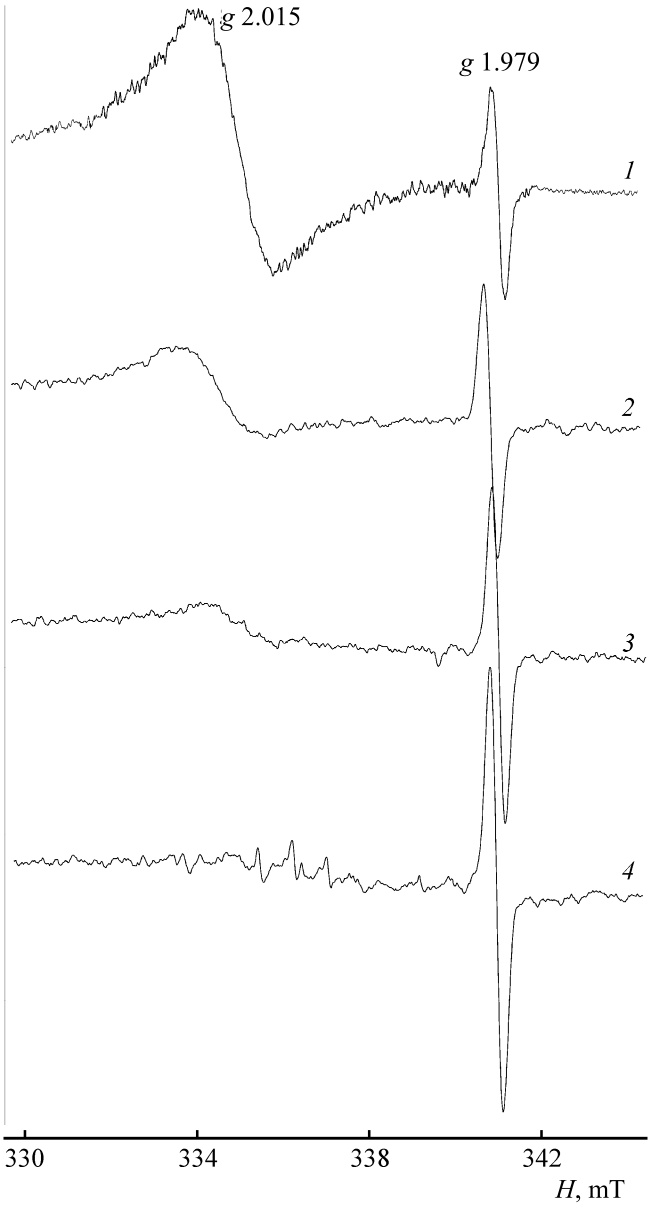


Fig. 2. ESR spectrum of tetra-*tert*-butoxychromium–*tert*-butyl hydroperoxide (1:10) in the presence of 2-methyl-2-nitrozopropane (C_6H_6, 20°C): (*1*) immediately after mixing, (*2*) 5 min after mixing, (*3*) 10 min after mixing, and (*4*) 25 min after mixing. Signal 1 assigned to Cr^V=O.

$R'N(O^{\bullet})Bu$-*t* (4) (Fig. 3). The structure of R and R' was not identified. We believe that the registered radicals were decomposition products of the chromium-containing peroxide.

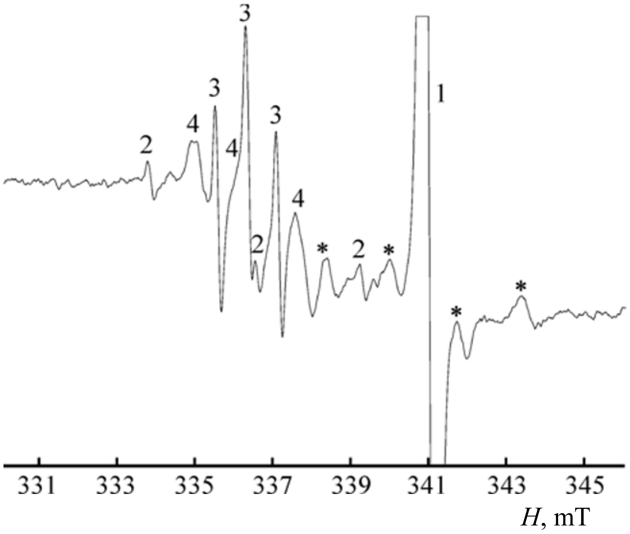


Fig. 3. ESR spectrum of (t-BuO)$_4$Cr–t-BuOOH (1:10) in the presence of 2-methyl-2-nitrozopropane (C_6H_6, 20°C), 25 min after mixing (enlarged). (*) Satellites of ^{53}Cr isotope. The numbers correspond to the assignments in the text.

After the introduction of *C*-phenyl-*N*-*tert*-butylnitrone to the reaction mixture [**II** : **I** = 1 : 10, C_6H_6, 20°C] with subsequent degassing of the solution, the ESR spectrum was registered containing three signals: a triplet (1 : 1 : 1), a triplet of doublets (1 : 1), and a singlet. The triplet signal with $g = 2.0066$ and $a_N = 0.79$ mT, following [12, 13], was assigned to the benzoyl-*tert*-butylnitroxyl $PhCON(O^{\bullet})Bu$-*t* (5), formed via oxidation of the spin trap with either singlet oxygen or peroxyl radical. The triplet-doublet signal with $g = 2.0061$, $a_N = 1.33$ mT, and $a_H = 0.138$ mT was assigned to the adduct of *C*-phenyl-N-*tert*-butylnitrone with peroxyl radical, most likely with *t*-butylperoxyl [12]. The singlet with $g = 1.979$ was assigned to chromyl Cr^V=O [9, 10].

Thus, in the reacting mixture of the alkoxide **II** and hydroperoxide **I**, we were able to identify the chromium-containing peroxide and alkoxide radicals, as well as *tert*-butylperoxide and *tert*-butoxide radicals; furthermore, formation of oxygen was confirmed.

The proposed scheme of Cr(OBu-*t*)$_4$ interaction with *t*-BuOOH is shown in Eqs. (1)–(5). Initially, the complex was formed; subsequently, nucleophilic substitution of *tert*-butoxy group with peroxide occurred:

$$(t\text{-BuO})_4\text{Cr} + t\text{-BuOOH} \rightarrow [(t\text{-BuO})_4\text{Cr}\cdot t\text{-BuOOH}] \xrightarrow{-t\text{-BuOH}} (t\text{-BuO})_3\text{CrOOBu-}t. \tag{1}$$

In the ^{1}H and ^{13}C NMR spectra of the 1 : 1 mixture of **I** and **II** (C_6D_6, 20°C, green solution), within 2 min a signal of *tert*-butanol appeared along with a broad peak of the (t-BuO)$_4$Cr protons (3.03 ppm). The chromium-containing peroxide decomposed to chromyl **A** [Eq. (2)]. The latter, having an unpaired electron in the π* molecular orbital, could account for the radical character of the Cr=O bond.

$$(t\text{-BuO})_3\mathrm{Cr^{IV}OOBu}\text{-}t \rightarrow t\text{-BuO}^{\cdot} + (t\text{-BuO})_3\mathrm{Cr^{V}{=}O}\ (\mathbf{A}). \quad (2)$$

When four moles of **I** was added to the above-described reaction mixture, the intensity of alcohol signals in the ^{1}H and ^{13}C NMR spectra increased, whereas the signal of chromium alkoxides got weaker. After 30 min, the latter signal virtually disappeared. As the amount of hydroperoxide increased, in the NMR spectra of the reaction mixtures the signals of *tert*-butyl peroxide, methyl *tert*-butyl ether, and acetone were identified, confirming the presence of *tert*-butoxide radicals.

Further interaction of chromyl **A** with hydroperoxide **I** probably occurred via several pathways. By analogy with the reactions of aluminum, titanium, zirconium, and vanadium alkoxides with *tert*-butyl hydroperoxide [3–5, 12], those might be the formation and decomposition of chromium trioxide [Eqs. (3)–(6)].

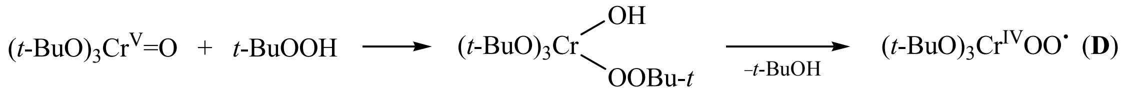
$$(t\text{-BuO})_3\mathrm{CrO} + t\text{-BuOOH} \longrightarrow t\text{-BuOH} + (t\text{-BuO})_2\mathrm{Cr(O)OOBu}\text{-}t\ (\mathbf{B}) \quad (3)$$

$$\mathbf{B} + t\text{-BuOOH} \longrightarrow (t\text{-BuO})_2\mathrm{Cr(O)OOOBu}\text{-}t\ (\mathbf{C}) \quad (4)$$

$$\mathbf{C} \longrightarrow \begin{cases} (t\text{-BuO})_3\mathrm{CrO} + \mathrm{O_2} \\ (t\text{-BuO})_2\mathrm{Cr(O)O}^{\cdot} + {}^{\cdot}\mathrm{OOBu}\text{-}t \\ (t\text{-BuO})_2\mathrm{Cr(O)OO}^{\cdot} + {}^{\cdot}\mathrm{OBu}\text{-}t \end{cases} \quad (5)$$

Substitution of the alkoxide group in chromyl **A** with *tert*-butylperoxyl group led to peroxide **B**, its subsequent reaction with **I** resulting in chromium-containing peroxytrioxide **C**. The latter decomposed with oxygen release, generating alkoxy and peroxyl radicals simultaneously. Recently, the experimental and theoretical evidence was obtained for the molybdenum(VI) trioxide formation in the reaction of molybdenum(VI) peroxide with alkylhydroperoxide. Homolysis of the trioxide also resulted in formation of alkoxy and peroxyl radicals, which were registered by ESR [14]. Decomposition of the trioxide **C** dimer should produce oxygen in the singlet state [3, 7].

Given the possibility of hydroperoxide addition at the Cr=O bond [1, 15], the reaction [Eq. (6)] leading to radical **D** could not be excluded.



$$(t\text{-BuO})_3\mathrm{Cr^{V}{=}O} + t\text{-BuOOH} \longrightarrow (t\text{-BuO})_3\mathrm{Cr}\begin{smallmatrix}\mathrm{OH}\\ \mathrm{OOBu}\text{-}t\end{smallmatrix} \xrightarrow[-t\text{-BuOH}]{} (t\text{-BuO})_3\mathrm{Cr^{IV}OO}^{\cdot}\ (\mathbf{D}) \quad (6)$$

$$\begin{aligned} &(t\text{-BuO})_3\mathrm{Cr^{IV}OO}^{\cdot} + {}^{\cdot}\mathrm{OOBu}\text{-}t \\ &\longrightarrow (t\text{-BuO})_3\mathrm{Cr^{IV}{-}OOOO{-}Bu}\text{-}t \\ &\longrightarrow (t\text{-BuO})_3\mathrm{Cr^{V}O} + \mathrm{O_2} + {}^{\cdot}\mathrm{OBu}\text{-}t \end{aligned} \quad (7)$$

Recombination of the peroxyl radicals according to Eq. (7) led to regeneration oxochromyl.

Furthermore, the elimination of hydrogen atoms induced by radical **D** followed by transformation of the hydroperoxide was possible [Eq. (8)].

$$\begin{gathered} (t\text{-BuO})_3\mathrm{Cr^{IV}OO}^{\cdot} + \mathrm{SH} \xrightarrow[-\mathrm{S}^{\cdot}]{} (t\text{-BuO})_3\mathrm{Cr^{IV}OOH} \longrightarrow (t\text{-BuO})_3\mathrm{Cr^{V}{=}O} + {}^{\cdot}\mathrm{OH} \xrightarrow{\mathrm{SH}} \mathrm{H_2O} \\ [\mathrm{Cr}]{-}\mathrm{OBu}\text{-}t + \mathrm{H_2O} \longrightarrow t\text{-BuOH} + [\mathrm{Cr}]{-}\mathrm{OH} \\ \mathrm{SH} = t\text{-BuOH},\ t\text{-BuOOH},\ {>}\mathrm{C{-}H}. \end{gathered} \quad (8)$$

tert-Butoxy radicals [Eqs. (2), (5), (7)] were converted into alcohol via detachment of hydrogen from both hydroperoxyl group and C–H bonds. The latter reaction explained the excessive yield of *tert*-

butanol, even at equimolar ratio of **I** to **II**. In excess of the hydroperoxide, the recombination of two *t*-BuOO• radicals should also lead to the release of oxygen.

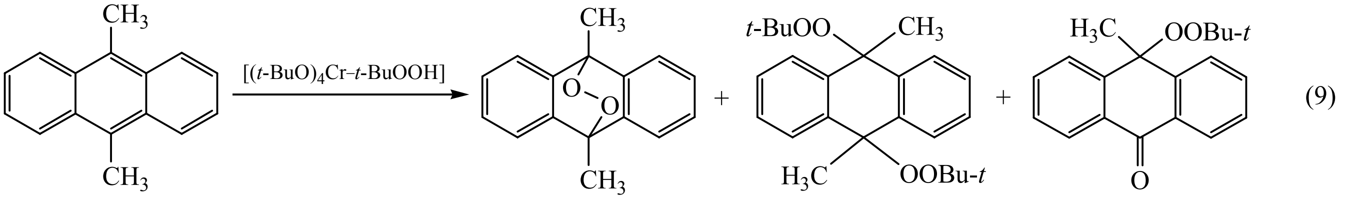
As noted above, the interaction with **I** could occur at different bonds of Cr–OBu-*t*. This was accompanied with formation of brown chromium-containing precipitates. In the IR spectra of the precipitates, the intensity of the C–O and C–H bands decreased, and a broad band appeared at 3150 cm^{-1} assigned to stretching of Cr–OH [10], along with the band at 945 cm^{-1} (Cr^{V}=O). The chromium content in the precipitates was of 25–30%.

In order to identify the nature of oxidants in the **I**+**II** system, we studied its interaction with 9,10-dimethylanthracene and with anthracene. The reactions were performed in benzene (20°C), at a molar ratio of 9,10-dimethylanthracene to the hydroperoxide of 1 : 3. The ratio of **II**:**I** was ranged from 1 : 3 to 1 : 30. The main products identified were 9,10-dimethyl-9,10-epidioxyanthracene **III**, 9,10-dimethyl-9,10-dihydro-9,10-di-*tert*-butylperoxyanthracene **IV**, 10-methyl-10-*tert*-butylperoxy-9-anthrone **V**, and methyl *tert*-butyl ether [Eq. (9) and Table 2].

Table 2. Products of 9,10-dimethylanthracene reaction with *t*-BuOOH–Cr(OBu-*t*)$_4$ system (C$_6$H$_6$, 20°C, 1 day), in moles per 1 mole of the substrate

Products of reaction	9,10-DMA:*t*-BuOOH:Cr(OBu-*t*)$_4$[a]	
	1:3:1	10:30:1
III	0.12	0.18
IV	0.05	0.28
V	0.28	0.16
MeOBu-*t*	0.29	0.15
t-BuOH	5.08	2.00
9,10-9,10-Dimethylanthracene (source)	0.36	0.15

[a] Molar ratio.



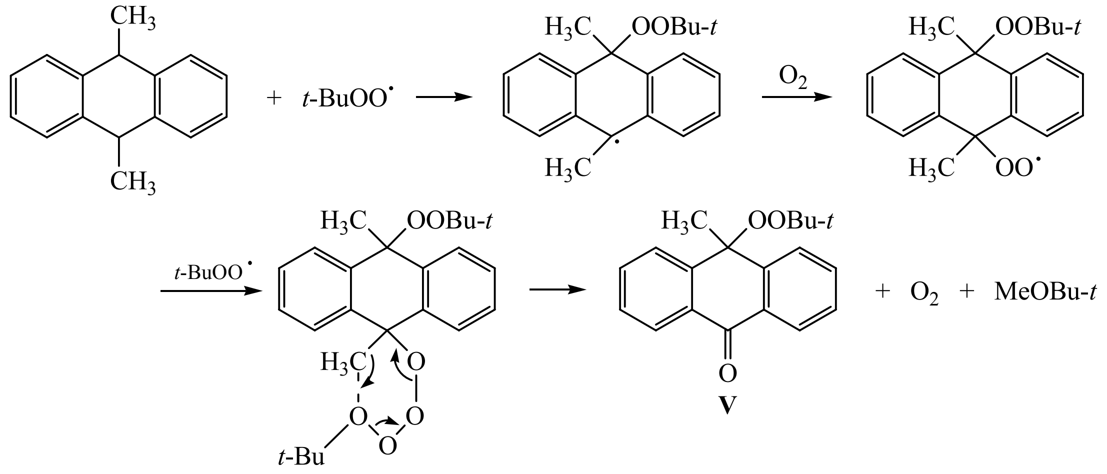
III **IV** **V** (9)

The peroxide **III** formation indicated the presence of either singlet oxygen or chromium trioxide [Cr–OO–OBu-*t*] in the system [7]. *tert*-Butylperoxyl groups at *meso* positions of **IV** indicated that peroxyl radicals were involved in the interaction. The process could be described by the scheme proposed for the reactions of 9,10-dimethylanthracene with *tert*-butyl hydroperoxide in the presence of cobalt, chromium, or vanadium acetylacetonates leading to peroxide **IV** [7]. Table 2 shows that the yield of **IV** increased when chromium alkoxide was used in catalytic amount, confirming the generation of peroxyl radicals from hydroperoxide **I**.

The third peroxy derivative product of that reaction was peroxyanthrone **V**, its amount formed was identical to that of methyl *tert*-butyl ether. It could be assumed that the carbonyl group was formed via decomposition of methyl *tert*-butylperoxyl group similar to the case of hydroperoxyl derivatives [16, 17]. However, diperoxyde **IV** was thermally stable [7] and was not converted into anthrone **V**. Likely, the peroxide **V** was formed via the molecular or homolytic decomposition of the tetraoxide, the product of two alkylperoxyl radicals dimerization [Eq. (10)].

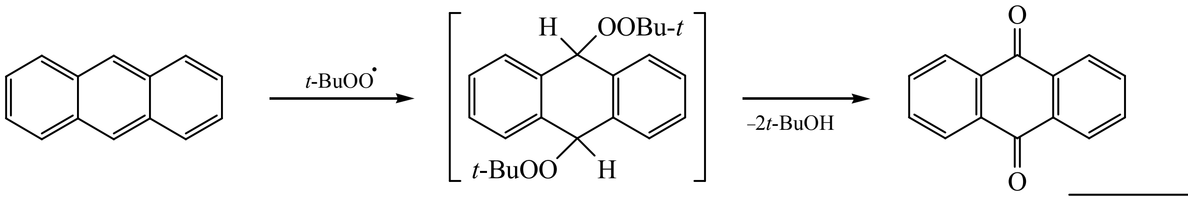
Reaction (10) could be facilitated by the nonlinear structure of the six-membered transition state.

The interaction of anthracene with the studied system led to anthraquinone, thus, oxidation of C–H bonds at the *meso* positions 9 and 10 occurred. The reaction conditions were similar to those given in Table 2. With the molar ratio of 1 : 3 : 1, anthraquinone yield was of 0.28 mol, reaching 0.38 mol when **II** was used in catalytic amount with respect to **I**. Conversion of anthracene was 30 and 40%, respectively. Either singlet oxygen, chromium trioxide (formed through the stage of epidioxy-9,10-anthracene), or *tert*-butylperoxy radicals could act as oxidant [7]. Given that



V

(10)



(11)

anthraquinone yield exceeded that of singlet oxygen (Table 1), the oxidation with *t*-BuOO˙ was most probable [Eq. (11)].

In the literature, anthracene conversion to quinone with quantitative yield by the action of *tert*-butyl hydroperoxide in the presence of bis(tributylstannyloxy)chromate (in 1,2-dichloroethane, 80°C) was described [18]. However, the reaction schemes were not presented, and the nature of the oxidant was unclear.

The arylalkenes containing only phenyl radicals and hydrogen atoms at the sp^2-hybrid carbon atoms were inert towards dissolved free singlet oxygen, but were oxidized with destruction of the double bond by metal complexes $^1O_2$ [19], metal-containing trioxides, or peroxyl radicals [7]. The reaction occurred via the stage of formation and decomposition of 1,2-dioxethanes. We studied the interaction of the **I**+**II** system with 1,1-diphenylethylene (Table 3). The major isolated products were benzophenone and the products of formaldehyde transformations. Formaldehyde was identified in the form of 2,4-dinitrophenylhydrazone, but in course of the reaction it was oxidized to formic acid and underwent the condensation transformations.

Table 3. Products of 1,1-diphenylethylene reaction with *t*-BuOOH–Cr(OBu-*t*)$_4$ system (C_6H_6, 20°C), in moles per 1 mol of the alkene

Products of reaction	$Ph_2C{=}CH_2$:*t*-BuOOH:Cr(OBu-*t*)$_4$[a]	
	1:4:1	10:40:1
Ph_2CO	0.50[b]	0.76
HCOOH[c]	0.29	0.12
$Ph_2C{=}CH_2$ (source)	0.21	0.16
t-BuOH[d]	2.29	2.54
t-BuOOH	–	1.23

[a] Molar ratio. [b] 1,1-Diphenyloxyrane also detected. After treatment with $BF_3{\cdot}OEt_2$, 2,2-diphenylethanal was identified.
[c] Formaldehyde detected. [d] In the volatile fraction.

Similarly to the reaction of phenylethenes with *t*-BuOOH in the presence of transition metal acetylacetonates [7], the oxidative degradation of 1,1-diphenylethylene likely occurred via formation of 1,2-dioxethane. The latter was produced in the reaction of phenylalkyl either with chromium compounds containing CrOOOBu-*t* or with the radical *t*-BuOO•. Possibly, both the oxidants were involved. Participation of *tert*-butylperoxyl radicals was indicated by presence of 1,1-diphenyloxyrane in the products.

Thus, in **I**+**II** system, oxygen (including its singlet form), chromium peroxytrioxide compounds, and *tert*-butylperoxyl radicals could act as oxidizers.

To clarify the oxidative capacity of the **I**+**II** system and to elucidate the transformation intermediates nature, we studied the interaction of **I**+**II** with alkylarenes and their selected oxygenated derivatives. In particular, the substrates were alkylarenes containing methyl, methylene and methine C–H bonds: ethylbenzene, *sec*-butylbenzene, and 1,1-diphenylalkanes Ph_2CHR (R = Me, Et).

Reactions with monophenylalkanes were performed in solution at 20°C (Table 4). As seen from Table 4, in the case of ethylbenzene the oxidation products maintaining the carbon backbone prevailed: acetophenone, 1-phenylethan-1-ol, 1-phenyl-1-hydroperoxyethane and unsymmetrical peroxide, the 1-phenyl-1-*tert*-butylperoxyethane. In the case of *s*-BuPh, the alcohol, hydroperoxide, and unsymmetrical peroxide were identified as well. In ethylbenzene, regardless of the **II** : **I** ratio (1 : 4 to 1 : 10) immediately after mixing the reactants and addition 2-methyl-2-nitrosopropane, ESR spectrum of the reaction mixture contained weak triplet of doublets with a_N = 1.48 mT, a_H = 0.36 mT, and g = 2.0051, assigned to the adduct of α-phenylethyl radical PhCH(Me)N(O•)Bu-*t* [12], and a strong singlet of chromyl (1) [g = 1.979 with satellite splitting with ^{53}Cr, $a(^{53}Cr)$ = 1.7 mT]. After 5–7 min, the radical adduct signal intensity decreased, and a new signal of *tert*-butoxy radical adduct appeared (2) (g = 2.0055, a_N = 2.72 mT). The intensity of the singlet did not change.

In the presence of *C*-phenyl-N-*tert*-butylnitrone, the ESR spectrum of **I**+**II** in ethylbenzene was a superposition of triplet, triplet of doublets, and singlet (Fig. 4). The triplet signal (1 : 1 : 1) was assigned to benzoyl-*tert*-butylnitroxyl radical according the isotropic parameters (g = 2.0066 and a_N 0.79 mT) (5). The signal of nitroxyl with g = 2.0061, a_N = 1.310 mT, and a_H = 0.101 mT was assigned to the adduct of *C*-phenyl-N-*tert*-1-butylnitrone with phenylethylperoxy radical PhCH(Me)OOCH(Ph)N(O•)Bu-*t* (6) [12]. The singlet was assigned to chromyl Cr^V=O (1). After 10 min, the intensity of chromyl signal increased and additional singlets with close but different the g-factors appeared. After 15 min, the signals of the peroxyl radical spin adduct (6) disappeared, the intensity of triplet (5) and the singlet with g = 1.979 increased, and a new signal, a triplet of doublets (a_N = 1.40 mT, a_H = 0.18 mT,a nd g = 2.0056) appeared assigned to the adduct of the spin trap with alkoxy radical PhCH(OR)·N(O•)Bu-*t* (R = PhCHMe or *t*-Bu) (7) [15, 20].

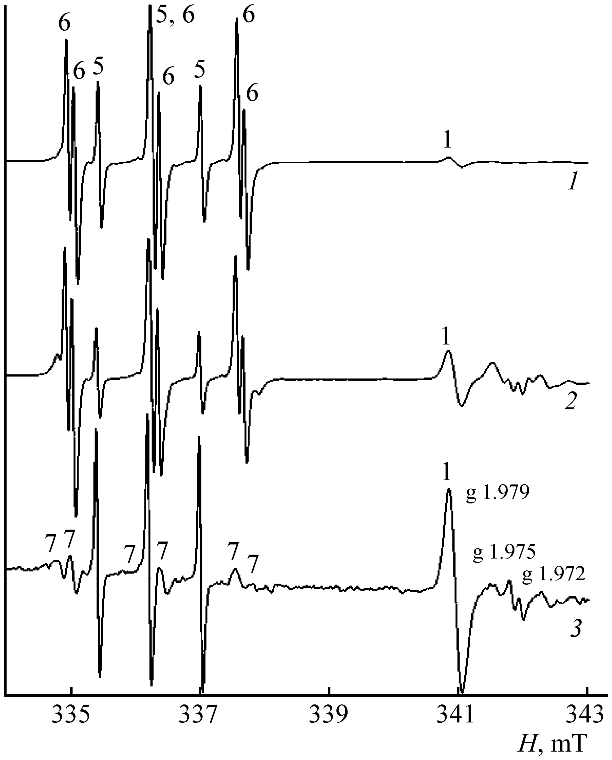


Fig. 4. ESR of tetra-*tert*-butoxychromium – *tert*-butyl hydroperoxide (1:8) (PhEt, 20°C) in the presence of C-phenyl-N-*tert*-butylnitrone: (*1*) immediately after mixing, (*2*) 10 min after mixing, and (*3*) 15 min after mixing. The numbers correspond to the assignments in the text.

The hydroperoxide-type conversion of methylene group into ketone one in the presence of CrO_3 was reported [1, 15, 20]. It was assumed that the oxidants involved were the chromium peroxy compounds, adducts of hydroperoxide and Cr=O bond. The scheme including formation and oxidation of a secondary alcohol was proposed to describe the transformation of the methylene C–H bonds to C=O group in benzyl, allyl, and propargyl fragments by *tert*-butylhydroperoxide [1, 15]. Similar processes could be assumed in the case of alkylarene reactions with **I**+**II**. However,

Table 4. Products of alkylarenes (PhR) oxidation with the *t*-BuOOH–Cr(OBu-*t*)$_4$ system (15:1, 20°C) in moles per 1 mol of the hydroperoxide

Products of reaction[a]	R=CH_2CH_3	R=$CH(CH_3)C_2H_5$
PhCHO	0.01	–[b]
Ketone	PhCOMe 0.52	PhCOMe 0.21
Alcohol	PhCH(OH)Me 0.26	PhC(Me)(Et)OH 0.14
Peroxide	PhCH(Me)OOBu-*t* 0.04	PhC(Me)(Et)OOBu-*t* 0.18
Hydroperoxide	PhCH(Me)OOH 0.04	PhC(Me)(Et)OOH 0.25

[a] Averaged. [b] Acetaldehyde detected. 0.06 moles of acetic acid found as well.

Table 5. Products of 1,1-diphenylalkanes reaction with *t*-BuOOH in the presence of $(t\text{-BuO})_4Cr$ and of 1-hydroperoxy-1,1-diphenylalkanes reaction with $(t\text{-BuO})_4Cr$ (C_6H_6, 20°C), in moles per 1 mol of hydrocarbon or hydroperoxide

Products of reaction	Ph_2CHR + *t*-BuOOH + $Cr(OBu\text{-}t)_4$[a]		$Ph_2C(R)OOH$ + $Cr(OBu\text{-t})_4$[b]	
	R = Me[c]	R = Et[c]	R = Me	R = Et
$Ph_2C(OH)R$	0.13	0.10	0.20	0.29
$Ph_2C(OOH)R$	0.02	0.08	0.11	0.20
Ph_2CO	0.01	0.07	0.01	0.40
PhCOR	0.29	0.20	0.61	0.09
PhOH	0.04	0.07	0.41	0.05
R'COOH	Traces[d]	0.03[e]	–[d]	0.16[e]

[a] The molar ratio of 10:30:1. [b] The molar ratio of 10:1. [c] Conversion of Ph_2CHMe 53%, Ph_2CHEt 55%. [d] R' = H. [e] R' = Me.

the ESR data along with the confirmed presence of oxygen, hydroperoxides, and unsymmetrical *tert*-butyl peroxides in the system indicated the homolytic way of their formation. Likely, the process was initiated by the oxygen-centered radicals [Eqs. (2) and (5)]. The carbon-centered radical reacted with oxygen. The subsequent transformation of peroxyl radicals (hydrogen detachment, formation and decomposition of tetraoxides, disproportionation according to the Russell scheme [21] in the case of PhCH (Me)OO• radicals) were responsible for the formation of compounds listed in Table 4. In the case of *sec*-butylbenzene, significant amounts of the products of carbon backbone destruction were identified: PhCOMe, CH_3COOH (acetaldehyde), and phenylethylketone (traces).

Destruction of the carbon backbone occurred in the case of **I**+**II** interaction with 1,1-diphenylalkanes Ph_2CHR (R = Me, Et) as well (Table 5). Tertiary hydroperoxides and alcohols, alkylphenylketones, benzo-phenone, and aldehydes or the corresponding acids (lesser amounts) were identified. Those compounds could result from transformations of tertiary alkylperoxyl radicals or metal peroxides [Eqs. (12)–(14)].

$$Ph_2CHR + XO^{\bullet} \xrightarrow[-XOH]{} Ph_2\dot{C}R \xrightarrow{O_2} Ph_2C(R)OO^{\bullet} \xrightarrow[-S^{\bullet}]{SH} Ph_2C(R)OOH \qquad (12)$$

$$2\,Ph_2C(R)OO^{\bullet} \xrightarrow[-O_2]{} 2\,Ph_2C(R)O^{\bullet} \xrightarrow[-S^{\bullet}]{SH} 2\,Ph_2C(R)OH \qquad (13)$$

X = *t*-Bu, *t*-BuO, [Cr], [Cr]O; R = Me, Et.

$$[Cr]\text{–}OOC(R)Ph_2 \longrightarrow [Cr]\text{–}OC(R)(Ph)OPh \longrightarrow [Cr]OPh + PhCOR \qquad (14)$$

Rearrangement with subsequent decomposition of alkylperoxyl radicals or chromium peroxide led to alkylphenylketones [Eq. (14)].

The presence of benzophenone could be attributed to decomposition of alkoxy radicals and recombination of alkylperoxyl radicals [22].

In order to confirm the role of hydroperoxides and peroxyl radicals in the oxidation of diphenylalkanes, we investigated the interaction of hydroperoxides $Ph_2C(R)OOH$ with alkoxide **II** in benzene. The reactants ratio was of 10 : 1, it should have led to high concentration of peroxyl radicals. The results presented in Table 5 confirmed participation of radicals $Ph_2C(OO^{\bullet})R$ in the formation of the specified products. The interaction of hydroperoxides with chromium alkoxide is represented by Eqs. (15) and (16).

$$R^1OOH + Cr(OBu\text{-}t)_4 \xrightarrow[-t\text{-BuOH}]{} (t\text{-BuO})_3CrOOR^1 \longrightarrow R^1O^{\bullet} + (t\text{-BuO})_3Cr{=}O \qquad (15)$$

$$R^1OOH + R^1O^{\bullet} \longrightarrow R^1OO^{\bullet} + R^1OH \qquad (16)$$

$R^1 = Ph_2CR^2$; R^2 = Me, Et.

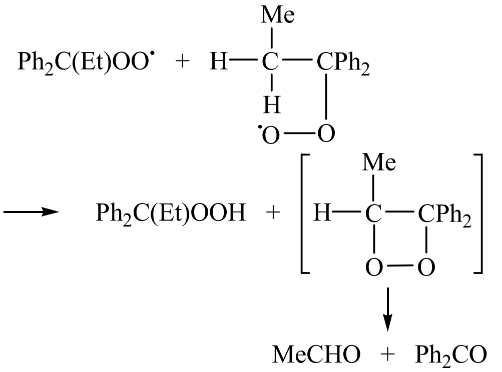
The ESR spectrum of reaction mixture [Eq. (16)] (R = Et, C_6H_6, 20°C) in the presence of *C*-phenyl-*N*-*tert*-butylnitrone contained triplet of doublets (5) assigned to nitroxyl oxidation product of the trap according to HFC, and triplet of doublets (8) with a_N = 1.36 mT, a_H = 0.18 mT, and $g = 2.0056$, characteristic of the spin trap adduct with alkoxy radicals PhCH(OR) N(O•)Bu-*t* [with RO• being likely $Ph_2C(O•)Et$]. In addition to signals (5) and (8), the spectrum contained a number of singlets with *g* of 1.970–1.979, assigned to oxochromyl group Cr^V=O, their intensity varying with time. After 13 min, a singlet with *g* = 1.972 prevailed (Fig. 5). It was reported that the *g*-factor of chromyl signal depended on the ligand environment of the metal [9–11]. Therefore, the reaction mixture contained several compounds $(RO)_3Cr^V$=O with different alkoxy groups. From Figs. 2–4, the signal with *g* = 1.979 was assigned to *tert*-butoxide derivative. Thus, the ESR data was in line with Eqs. (15) and (16).

As seen from Table 5, the quantitative composition of the products mixture was determined by the structure of the R in the starting hydroperoxide. In the case of 1-hydroperoxy-1,1-diphenylethane, the major product was acetophenone [Eq. (14)], whereas in the case of $Ph_2C(OOH)Et$ benzophenone prevailed. The increase of benzophenone yield was 40-fold, and could not be explained by higher stability of ethyl radical [Eq. (17)].

$$Ph_2C(O^{\cdot})R \rightarrow Ph_2CO + R^{\cdot} \qquad (17)$$

$$R = Me, Et.$$

Likely, the main pathway of benzophenone formation was recombination of alkylperoxyl radicals to form hydroperoxide and dioxethane. The latter decomposed into benzophenone and acetaldehyde, partially oxidized to acid [Eq. (18)].


(18)

The probability of reaction (18) in the case of $Ph_2C(Me)OO•$ should be much lower, due to stronger C–H bond of methyl group as compared with the methylene one, and to lower stability of methyl radical. The main transformation pathway of $Ph_2C(Me)OO•$ was formation of alkoxy radicals and rearrangement to acetophenone and phenol. The equation of type [Eq. (18)] could also account for the presence of acetophenone in the products of *s*-BuPh oxidation (Table 4).

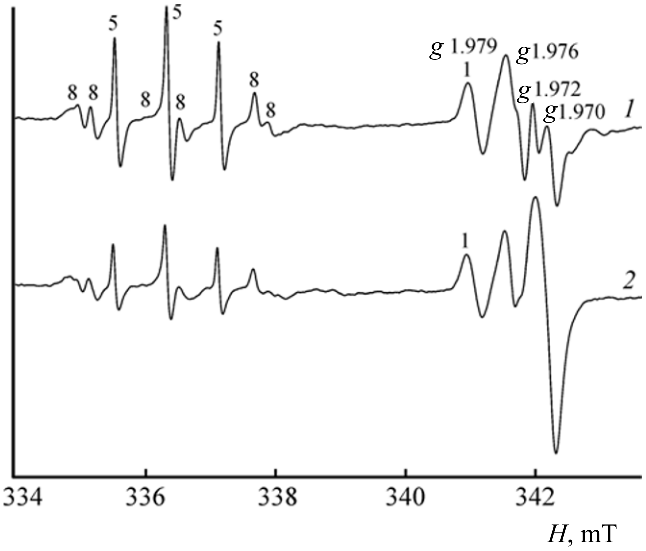


Fig. 5. ESR spectrum of tetra-*tert*-butoxychromium–1-hydroperoxy-1,1-diphenylpropane (1:8) in the presence of *C*-phenyl-*N*-*tert*-butylnitrone (C_6H_6, 20°C): (*1*) 1 min after mixing, (*2*) 13 min after mixing. Signal 5: adduct with benzoyl radical, signal 8: adduct with $Ph_2C(O^{\cdot})Et$ radical.

Thus, the interaction of alkylarenes with **I**+**II** system included the steps of formation of substrates peroxyl radicals, their transformation to the final oxidation products being possible both with and without destruction of the carbon backbone. The latter process involved the formation of intermediate 1,2-dioxethanes.

The ability of C–H bonds to be homolytically oxidized depends on the α-substituent structure, decreasing in the presence of electron-acceptor groups. We performed the interaction of methyl phenylacetate with **I**+**II** at the reagents ratios of 1 : 4 : 1 and 10 : 30 : 1 (catalytic mode, benzene, 20°C). The only isolated product was methyl benzoylformate with yield of 0.22 and 0.41 mol, respectively. Possibly, the α-hydroxy acid ester intermediate was formed, capable of subsequent transformation into keto ester. The alkoxide **II** was reported to oxidize primary alcohols [8], but at $Cr(OBu\text{-}t)_4$ to RCH_2OH ratio of 2 : 7 the aldehyde yield was less than 1 mol (14%).

We performed oxidation of ethyl 2-hydroxy-2-phenylethanoate with **I**+**II** system. The reaction conditions were the same as described above in $PhCH_2COOMe$ reaction. Ethyl benzoylformate was

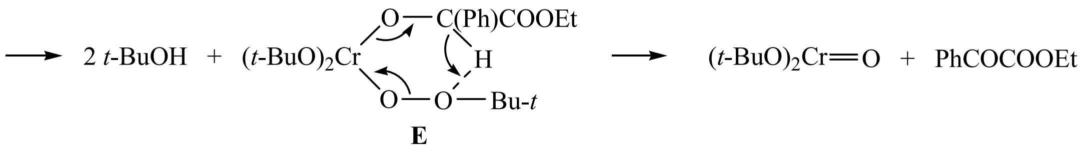
Table 6. Products of alcohols (ROH) oxidation with the t-BuOOH–Cr(OBu-t)$_4$ system (C_6H_6, 20°C), in moles per 1 mole of alcohol

Products of reaction	PhCH(OH)Me		$PhCH_2OH$		n-BuOH	
	1:4:1[a]	10:30:1[a]	1:4:1[a]	10:30:1[a]	1:4:1[a]	10:30:1[a]
Carbonyl compound	0.98	0.75	0.84	0.38	0.07[b]	Traces[b]
R'COOH	–	–	0.15[c]	0.60[c]	0.56[d]	0.38[d]
t-BuOH	5.12	1.30	4.52	1.81	5.77	2.37
ROH (source)	–	0.17	–	–	–	0.38

[a] The molar ratio of ROH:t-BuOOH:Cr (OBu-t)$_4$. [b] The products of butanal condensation. [c] R '= Ph. [d] R '= Pr.

isolated (0.99 and 0.66 mol, respectively). The highest conversion of $PhCH_2COOMe$ was achieved with catalytic amount of **II** and equimolar amount of PhCH·(OH)COOEt. Given that fact, and taking into account the data published on secondary alcohols oxidation with CrO_3–t-BuOOH [1, 23, 24], we proposed the intramolecular mechanism involving six-membered intermediate complex [Eq. (19)].

$$(t\text{-BuO})_4Cr + t\text{-BuOOH} + PhCH(OH)COOEt$$



E

(19)

In the catalytic mode, the catalyst could regenerate via addition of hydroperoxide at the Cr=O bond [Eq. (20)].

$$[Cr]{=}O + t\text{-BuOOH} \rightarrow [Cr](OH)OOBu\text{-}t$$
$$+ PhCH(OH)COOEt \rightarrow H_2O + \mathbf{E}. \qquad (20)$$

Water hydrolyzed the Cr–OBu-t bond leading to composition of the alkoxide and precipitation of the hydrolysis products, thus yield of the benzoylformate was decreased.

Similar results were obtained in oxidation of 1-phenylethan-1-ol with **I**+**II**. Oxidation of primary alcohols under identical conditions led to aldehydes [Eq. (19)] and carboxylic acids (Table 6). The final product yield depended on the structure of alcohol and the ratio of initial reagents. Conversion of aldehydes into acid could be initiated by in situ generated oxygen, or by chromium peroxy compounds, similarly to the cases of aluminum and titanium derivatives [25, 26] [Eq. (21)].

$$[Cr]OOBu\text{-}t + RCHO \rightarrow [Cr]OCH(R)OOBu\text{-}t$$
$$\rightarrow [Cr]OCOR + t\text{-BuOH}. \qquad (21)$$

Consequently, chromium-containing peroxy compounds participated in the oxidation of primary and secondary alcohols, as well as of aldehydes.

EXPERIMENTAL

The reaction products were analyzed by GLC, TLC, IR, ESR, ^1H and ^{13}C NMR, and electron spectroscopy. Electronic absorption spectra were recorded at room temperature with Shimadzu UV-1800 unit. IR spectra were recorded with Shimadzu IR Prestige-21 device (KBr tablets or thin layer). ESR spectra were recorded with Bruker EMX spectrometer, at operating frequency of 9.75 GHz, with diphenylpicrylhydrazyl as g-factor reference. To improve the resolution of ESR spectrum and to remove oxygen, the solutions were degassed. Chromium alkoxide concentration was of 0.005 mol/L. ^1H and ^{13}C NMR spectra were recorded with Agilent DD2 NMR 400 spectrometer at operating frequencies of 400 and 101 MHz, respectively. Chemical shifts were reported as δ relative to Me_4Si.

Chromatographic analysis of the reaction products in the liquid phase was carried out with Shimadzu GC-2010A device equipped with a flame ionization detector and capillary column Equity-5, 30000× 0.32 mm; with nitrogen as carrier gas. The content of the mixture components was determined at the following temperatures: benzaldehyde, acetophenone, phenylethylketone, 1-phenylethan-1-ol, 2-phenylbutan-

2-ol, and methyl benzoate at 130ºC; *tert*-butyl peroxide, *tert*-butanol, *tert*-butyl acetate, methyl *tert*-butyl ether, and *n*-butanol at 50ºC; $PhCH_2COOMe$, PhC(O)· COOMe, PhCH(OH)COOEt, PhC(O)COOEt, Ph_2CHMe, Ph_2CHEt, $Ph_2C(OH)Me$, $Ph_2C(OH)Et$, Ph_2CO, PhCH(Me)OOBu-*t*, PhC(Me)(Et)OOBu-*t*, $Ph_2C{=}CH_2$, and PhOH at 170–180ºC. The analysis was always performed using external reference compounds. To isolate the products by column chromatography, silica gel 60 (0.06–0.2 mm) was used as adsorbent.

Quantitative analysis of hydroperoxides was performed by iodometric titration. Carboxylic acids were identified and analyzed in the form of methyl esters after treatment with diazomethane. Carbonyl compounds were identified in the form of 2,4-dinitrophenylhydrazones according to melting point and TLC R_f values using the reference substances. Sorbent used was Silpearl, a wide porous silica gel on aluminum foil (Silufol UV-254); the eluent was carbon tetrachloride–diethyl ether 9 : 1. The chromium content was determined by the Palmer method [27].

Tetra-*tert*-butoxychromium was synthesized according to [28]. Found, %: Cr 15.14, $C_{16}N_{36}O_4Cr$. Calculated, %: Cr 15.09. Spectral characteristics of the alkoxide coincided with the literature data [8].

1,1-Diphenylalkanes Ph_2CHR were obtained by alkylation of benzene with corresponding alcohols. R = Me, bp 114–115ºC (4 mm Hg), n_D^{21} 1.5740; R = Et, bp 130–132ºC (4 mm Hg), n_D^{20} 1.5630 [29]. Tertiary alcohols $Ph_2C(OH)R$ (R = Me, Et) were synthesized using organomagnesium compounds [30], their constants corresponded to the published data. 1-Hydroperoxy-1,1-diphenylethane and 1-hydroperoxy-1,1-diphenylpropane were obtained by treating the corresponding alcohols with 88% H_2O_2 in ether in the presence of conc. H_2SO_4 at 0–5ºC. $Ph_2C(OOH)Me$ was purified by precipitation with petroleum ether from the concentrated ether solution, mp 85°C; $Ph_2C(OOH)Et$ was twice recrystallized from hexane, mp 80ºC [31]. 1-*tert*-Butylperoxy-1-phenylethane was synthesized from α-phenylethylbromide and potassium salt of *tert*-butyl hydroperoxide, bp 56ºC (1 mm Hg), n_D^{20} 1.4810 [32]. 2-*tert*-Butylperoxy-2-phenylbutane was obtained via reaction of 2-phenylbutan-2-ol with *tert*-butyl hydro-peroxide in glacial acetic acid, the catalyst was conc. H_2SO_4, bp 60–62ºC (1 mm Hg), n_D^{20} 1.4780 [33]. Phenylacetic acid methyl ester was obtained by esterification in the presence of $POCl_3$ [34], bp 215°C, n_D^{23} 1.5055 [35]. The concentration of *tert*-butyl hydroperoxide was more than 99.6–99.8%. We used the following commercial reagents: *sec*-butylbenzene (99%), ethyl-D,L-mandelate (97%), 1,1-diphenylethylene (98%) (all – Acros Organics), and 9,10-dimethylanthracene (98%, TCI Europe nv).

Interaction of chromium tetra-*tert*-butoxide with *tert*-butyl hydroperoxide (1 : 10) in benzene, 20°C. 0.41 g of *t*-BuOOH was added to 0.158 g of Cr(OBu-*t*)$_4$ in 12 mL of benzene. The reaction was exothermic. The color of the reaction mixture immediately changed from sky blue to dark orange. After 20 h, the solution was pale orange, and dark brown precipitate was found at the flask bottom. The precipitate was filtered off, dried (0.0183 g), and analyzed. Its IR spectrum contained absorption bands at ν, cm^{-1}: 3400 (Cr–OH), 944 (Cr=O), 820, 520 (Cr–O–Cr), 1627 (H_2O crystallization). The solvent and volatile components of the filtrate were condensed in a trap cooled with liquid nitrogen. The residue was a dark brown solid, the band at 945 cm^{-1} ($Cr^V{=}O$) dominated in its IR spectrum. In the condensate (yellow), *t*-BuOH (0.36 g), *tert*-butyl peroxide (0.018 g), MeOBu-*t* (0.005 g), and Cr (0.010 g) were found. An aliquot of the condensate was treated with triphenylphosphine till discoloration of the solution, after that 0.051 g of Ph_3PO was determined.

In the parallel experiments, an aliquot of the condensate was heated (70°C, 5 h) with acetic acid, a four-fold amount with respect to the chromium alkoxide. In the solution, 0.40 g of *t*-BuOH and traces of *tert*-butyl acetate were found. The difference between the amount of alcohol in the volatile fraction before and after treatment with acid (0.04 g) indicated the presence of the volatile chromium compounds in the condensate. [Cr] : [*t*-BuO] : [Cr=O] = 1 : 2.84 : 0.92, close to (*t*-BuO)$_3$CrO.

The amount of oxygen was determined in a separate experiment using the method [6].

Interaction of 9,10-dimethylanthracene with *tert*-butyl hydroperoxide in the presence of Cr (OBu-*t*)$_4$ (10 : 30 : 1). 0.27 g of *t*-BuOOH was added to 0.034 g of chromium alkoxide and 0.20 g of 9,10-dimethylanthracene in 25 mL of benzene. The solution became dark brown immediately, with fine dark brown precipitate formed. After 20 h, the precipitate that contained chromium was filtered off. The solvent and volatile products in the filtrate (*t*-BuOH, 0.15 g; MeOBu-*t*, 0.014 g; *t*-BuOOH, 0.034 g) were condensed in a trap cooled with liquid nitrogen. The residue was analyzed by column chromatography, the eluent was benzene. The course of the analysis was monitored by TLC (benzene, then treatment with solution of phosphomolybdic acid and heating). Four fractions were identified: (1) unreacted 9,10-dimethylanthracene (0.032 g), mp 182–183°C; (2) *trans*-diperoxyde **IV**, 0.11 g, after washing with cold (0–5°C) ethanol, mp 113°C, mp, IR, and NMR (^{1}H, ^{13}C, $CDCl_3$) data were identical to the published [7]; (3) isolated yellow crystalline solid (0.047 g); IR spectrum (KBr), ν, cm^{-1}: 3068, 3034, 2976, 2927, 2861, 1667 (>C=O), 1604 (C=C), 1459, 1362, 1319, 1290, 1196, 1157, 1076, 932, 883, 760, 688; ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.16 [9H, $C(CH_3)_3$], 1.63 [3H, CH_3], 7.45–8.29 [8H, Ph, 7.47–7.49 m, 7.64–7.68 m, 7.84–7.86 d, 8.27–8.29 d]; ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 26.81 [$C(CH_3)_3$], 33.41 (CH3), 78.31 [$C(CH_3)_3$], 79.63 ($CH_3\underline{C}$–O), 131.05, 146.71 (condensed rings), 126.53, 127.14, 127.77, 133.22 (Ph), 183.67 (>C=O), mp 97–98°C. According to IR and NMR spectroscopy, the product (3) was 10-methyl-10-*tert*-butylperoxy-9-anthrone **V**. The presence of the carbonyl group was confirmed by reaction with 2,4-dinitrophenylhydrazine. Treatment with NaI in acetic acid (60°C, in a sealed tube) resulted in release of iodine. Found, %: O (active) 5.17. $C_{19}N_{20}O_3$. Calculated, %: O (active) 5.40. After a month storage (20°C), the compound **V** converted into anthraquinone. Fraction (4): 0.043 g of epidioxyanthracene **III**. After washing with ethanol (0–5°C) colorless crystals were isolated, mp 219°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.14 (6H), 7.2–7.4 m (8H). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 13.70, 79.50, 120.65, 127.37, 140.71.

Interaction of *tert*-butyl hydroperoxide with chromium tetra-*tert*-butoxide in ethylbenzene (15 : 1, 20°C). 0.20 g of *t*-BuOOH was added to 0.05 g of alkoxide **II** in 10 mL of ethylbenzene. The reaction solution immediately turned bright red, and after 20 min it became orange. Next day, the solution was yellowish, with dark brown precipitate at the bottom. IR spectrum of the precipitate was identical the case of the reaction in benzene (10 : 1). The liquid phase was decanted. Volatile products and solvent were condensed in a trap cooled with liquid nitrogen. The residue (brown mass) was hydrolyzed with 10% H_2SO_4, extracted with ether, and dried over Na_2SO_4. In the condensate and the hydrolyzate, 0.012 g of 1-hydroperoxy-1-phenylethane, 0.16 g of acetophenone, 0.08 g of 1-phenylethan-1-ol, 0.015 g of 1-*tert*-butylperoxy-1-phenylethane, and 0.002 g of benzaldehyde were identified. 0.30 g of *tert*-butyl alcohol was also found in the condensate.

To quantify 1-hydroperoxy-1-phenylethane, an aliquot of the reaction solution was treated with excess of triphenylphosphine. Amount of the hydroperoxide was determined by the difference of 1-phenylethan-1-ol amount.

Oxidation of ethyl 2-hydroxy-2-phenylethanoate with the *t*-BuOOH-(*t*-BuO)$_4$Cr system (1 : 4 : 1, benzene, 20°C). A mixture of 0.26 g of (*t*-BuO)$_4$Cr, 0.27 g of *t*-BuOOH, and 0.14 g of the ester in 10 mL of benzene was kept at room temperature during 20 h. The reaction solution became dark brown. It was decanted from the insoluble precipitate of chromium compounds. The liquid phase was treated as described above. In the volatile fraction, 0.37 g of *t*-BuOH and 0.012 g of (*t*-BuO)$_2$ were found. In the aqueous acid extract 0.004 g of H_2O_2 was found. In the ether extract, 0.004 g of unreacted ether and 0.23 g of ethyl benzoylformate were identified. After treating the reaction mixture with 2,4-dinitrophenylhydrazine, 2,4-dinitrophenylhydrazones of two of ethyl benzoylformate isomers were isolated by column chromatography (eluent $CCl_4 : Et_2O = 9 : 1$) : *Z*-isomer, mp 158°C and *E*-isomer, mp 144°C. Structure of the hydrazones was confirmed by IR and UV spectroscopy. IR spectrum (CCl_4), ν, cm^{-1}: *Z*-form, 3210 [ν(N–H)], 1697 [ν(C=O)]; *E*-form, 3280 [ν(N–H)], 1722 [ν(C=O)]. UV (EtOH), λ_{max}, nm: *Z*-form, 384.5 nm; *E*-form, 357.5 nm.

The experiments and analysis of the reaction products not listed in the experimental part were performed similarly.

ACKNOWLEDGMENTS

The authors thank Yu.B. Malysheva for registration of NMR spectra and assistance in their interpretation.

REFERENCES

1. Muzart, J., *Chem. Rev.*, 1992, vol. 92, no. 1, p. 113.
2. Muzart, J., *Synthesis*, 1993, no. 1, p. 11.
3. Stepovik, L.P., Gulenova, M.V., Martynova, I.M., Mar'yasin, B.A., and Cherkasov, V.K., *Russ. J. Gen. Chem.*, 2008, vol. 78, no. 2, p. 266.
4. Gulenova, M.V., Stepovik, L.P., and Cherkasov, V.K., *Russ. J. Gen. Chem.*, 2006, vol.76, no. 6, p. 980.
5. Stepovik, L.P., Gulenova, M.V., Tishkina, A.N., and Cherkasov, V.K., *Russ. J. Gen. Chem.*, 2007, vol. 77, no. 7, p. 1254.
6. Stepovik, L.P. and Gulenova, M.V., *Russ. J. Gen. Chem.*, 2009, vol. 79, no. 8, p. 1663.

7. Stepovik, L.P., Potkina, A.Yu., and Poddel'skii, A.I., *Russ. J. Gen. Chem.,* 2012, vol. 82, no. 9, p. 1473.
8. Alyea, E.C., Basi, J.S., Bradley, D.C., and Chisholm, M.H., *J. Chem. Soc. (A),* 1971, part 1, p. 772.
9. O'Reilly, M., Falkowski , J.M., Ramachandran, V., Pati, M., Abboud, K.A., Dalal, N.S., Gray, T.G., and Veige, A.S., *Inorg. Chem*., 2009, vol. 48, no. 23, p. 10901.
10. Groysman, S., Villagran, D., and Nocera, D.G., *Inorg. Chem*., 2010, vol. 49, no. 23, p. 10759.
11. Egorova, O.A., Tsay, O.G., Khatua, S., Huh , J.O., and Churchill, D.G., *Inorg. Chem*., 2009, vol. 48, no. 11, p. 4634.
12. Stepovik, L.P., Martynova, I.M., Dodonov, V.A., and Cherkasov, V.K., *Russ. Chem. Bull*., 2002, no. 4, p. 638.
13. Zubarev, V.E., *Metod spinovykh lovushek. Primenenie v khimii, biologii, meditsine* (Method of Spin Traps. Application in Chemistry, Biology, and Medicine), Moscow: Mosk. Gos. Univ., 1984.
14. Neuenschwander, U., Meier, E., and Hermans, I., *Chem. Eur. J*., 2012, vol. 18, p. 6776.
15. Muzart, J. and Piva, O., *Tetrahedron Lett*., 1998, vol. 29, no. 19, p. 2321.
16. Glushakova, V.N., Skorodumova, N.A., Nevodchikov, V.I., Abakumova, L.G., Makarenko, N.P., Cherkasov, V.K., and Druzhkov, O.N., *Russ. Chem. Bull*., 1999, no. 5, p. 934.
17. Stepovik, L.P., Gulenova, M.V., Shavyrin, A.S., and Fukin, G.K., *Russ. J. Gen. Chem*., 2006, vol. 76, no. 8, p. 1275.
18. Muzart , J., *Synth. Commun*., 1989, vol. 19, nos. 11–12, p. 2061.
19. Gekhman, A.E., Amelichkina, G.E., Moiseeva, N.I., Vargaftik, M.N., and Moiseev, I.I., J. *Mol. Catal. (A)*, 2000, vol. 62, no. 1, p. 111.
20. Glushakova, V.N., Skorodumova, N.A., Gryzina, O.Yu., Domrachev, G.A., Aleksandrov, Yu.A., and Razuvaev, G.A., *Kinetika i Kataliz,* 1989, vol. 30, no. 3, p. 656.
21. Russell, G.A., *J. Am. Chem. Soc*., 1957, vol. 79, no. 14, p. 3871.
22. *Stepovik, L.P. and Potkina, A.Yu., Russ. J. Gen. Chem*., 2013, vol. 83, no. 6, p. 1047
23. Muzart, J., *Tetrahedron Lett*., 1987, vol. 28, no. 19, p. 2133.
24. Riahi, A., Hénin, F., and Muzart, J., *Tetrahedron Lett*., 1999, vol. 40, no. 12, p. 2303.
25. Dodonov, V.A., Stepovik, L.P., Cofronova, S.M., and Grishin, D.F.*, Zh. Obshch. Khim*., 1983, vol. 53, no. 11, p. 2527.
26. Stepovik, L.P., Gulenova, M.V., and Martynova, I.M., *Russ. J. Gen. Chem*., 2005, vol. 75, no. 4, p. 507.
27. Palmer, W.G., *Experimental Inorganic Chemistry*, Cambridge: Cambridge University Press, 1954, p. 385.
28. Krauss, H.-L. and Münster, G., *Z. Anorg. Allgem. Chem*., 1967, vol. 352, no. 1, p. 24.
29. *Dictionary of Organic Compounds,* Moscow: Inostrannaya Literatura, 1949, vol. 1.
30. *Preparativnaya organieskaya khimiya* (Preparative Organic Chemistry), Moscow: Goskhimizdat, 1959, p. 647.
31. Davies, A.G., *Organic Peroxides*, London: Butterworths, 1961, p. 17.
32. Kornblum, N. and DeLaMare, H.E., *J. Am. Chem. Soc.*, 1952, vol. 74, no. 12, p. 3079.
33. Davies, A.G., Foster, R.V., and White, A.M., *J. Chem. Soc*., 1954, no. 7, p. 2200.
34. Weigand-Hilgetag, *Organishe-Chemishe Experimintierkust*, Moscow: Khimiya, 1968, p. 235.
35. *Aldrich, Catalogue Handbook of Fine Chemicals*, 1999–2000, Germany DM, p. 1184.